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## REEXAMINATION OF HIBSCHITE

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### ABSTRACT

X-ray powder patterns of hibsichte from the type locality at Aussig, Bohemia, closely resemble patterns of grossularite and plazolite. This confirms the suggestion of Belyankin and Petrov that it is nearly identical with plazolite. The conclusion is inescapable that hibsichte does not have the composition usually assigned to it.

### INTRODUCTION

Hibsichte was discovered by Cornu<sup>1</sup> as octahedral mantles about minute fragments of garnet in inclusions in phonolite at Marienberg, near Aussig, Bohemia. Cornu also identified dodecahedral mantles about melanite from Aubenas, Vivarais, France, previously called garnet by Lacroix,<sup>2</sup> as "hibsichte." Cornu was unable to separate hibsichte from its associated minerals, especially the enclosed garnet, for analysis. Instead he tried to determine its composition by analyzing it together with the enclosed kernels of garnet and deducting from this bulk analysis the composition of the kernels which were also analyzed separately. In this way he derived a formula for hibsichte identical with that of lawsonite, and it has since been assigned this formula in innumerable text- and reference books. A year later Cornu<sup>3</sup> found hibsichte at a similar locality, the Mädstein, near Neschwitz, Bohemia, but obtained no further information on its composition.

Hibsichte was next reported by Belyankin and Petrov,<sup>4</sup> again as mantles about garnet, from a marl and teschenite contact near Nikortz-minda, Georgia. For the hibsichte they found  $n_{Na} = 1.681$  and  $G. = 3.06$ , and for the enclosed garnet  $n = 1.815$  and  $G. = 3.68$ . No analysis was given.

<sup>1</sup> Cornu, F., Hibsicht, ein neues Kontaktmineral: *Tschermak's min., pet. Mitt.*, **25**, 249-268 (1906).

<sup>2</sup> Lacroix, A., Les enclaves des roches volcaniques, 149 (1893).

<sup>3</sup> Cornu, F., Ueber einen Kontakt zwischen Phonolith und oberturonem Kreidemergel am Mädstein bei Neschwitz a. d. Elbe: *Tschermak's min., pet. Mitt.*, **26**, 457-468 (1907).

<sup>4</sup> Belyankin, D. S., and Petrov, V. P., Hibsichte in Georgia: *Comptes Rendus (Doklady) de l'Academie des Sciences de l'URSS*, **24**, no. 4, 349-352 (1939).

Belyankin and Petrov also examined some of the hibschite from Aussig, Bohemia, and reported that the index of the enclosed garnet varies from 1.815, at the core, to 1.808 at the rim, and that its specific gravity is 3.61. They obtained no new data on the properties of the original hibschite but they reviewed Cornu's analyses and showed that they are not in harmony with the properties of the hibschite and the enclosed garnet.

Later Belyankin and Petrov<sup>5</sup> reported analyses of hibschite concentrates from which they derived the formula,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . This is the same formula as that used for plazolite by the writer<sup>6</sup> in his work on the crystal structure of that mineral. Belyankin and Petrov concluded that hibschite and plazolite are both members of the same mineral group for which they proposed the name *grossularoid group* because of the established close relationship of plazolite and grossularite.<sup>7</sup> Incidentally they reported another locality for "grossularoid", the fifth or sixth, in the Lopan gorge, southern Osetia, Transcaucasia.

In the main the writer is in accord with the conclusions of Belyankin and Petrov, but certain apprehensions they express concerning the relations of plazolite and hibschite require comment. They state that "plazolite differs only by a small and rather variable content of  $\text{CO}_2$ ," and in a foot-note, "the role of  $\text{CO}_2$  in plazolite is not quite clear." In my work on the structure of plazolite, I disregarded the  $\text{CO}_2$  content shown in the analyses. Soon thereafter I received some extended comments from Foshag, who had made the analyses, ending in the statement "the  $\text{CO}_2$  was in all probability due to admixture."<sup>8</sup> Belyankin and Petrov are also concerned about "the fact that plazolite is of a somewhat yellowish color" since iron oxides are absent in the analysis. Actually it was described by Foshag<sup>9</sup> as "colorless to light yellow." Such faint color as appears in some plazolite certainly does not indicate the presence of any important amounts of coloring constituents.

In Table 1 are given the analyses of plazolite from Crestmore and hibschite from Nikortzmindia for comparison with the ideal analysis corresponding to the formula assigned to these materials. It is seen that the hibschite analysis agrees fairly well if ferric oxide is grouped with alumina.

<sup>5</sup> Belyankin, D. S., and Petrov, V. P., The grossularoid group (hibschite, plazolite): *Am. Mineral.*, **26**, 450-453 (1941).

<sup>6</sup> Pabst, A., The crystal structure of plazolite: *Am. Mineral.*, **22**, 861-868 (1937).

<sup>7</sup> Recently the name *garnetoid* has been similarly used by Duncan McConnell, *Am. Mineral.*, **27**, 452-461 (1942).

<sup>8</sup> Personal communication from W. F. Foshag, dated July 23, 1937.

<sup>9</sup> Foshag, W. F., Plazolite, a new mineral: *Am. Mineral.*, **5**, 183-185 (1920).

TABLE 1

	I	II	III
SiO <sub>2</sub>	27.57	25.71	28.18
TiO <sub>2</sub>	0.67	—	—
Al <sub>2</sub> O <sub>3</sub>	18.52	25.27	23.91
Fe <sub>2</sub> O <sub>3</sub>	3.70	—	—
FeO	0.15	—	—
MnO	0.08	—	—
CaO	38.39	39.75	39.46
MgO	2.13	trace	—
H <sub>2</sub> O—	0.29	9.27	8.45
H <sub>2</sub> O+	8.55		
	100.00	100.00	100.00

I. Hibsichte, Nikortzinda, Georgia, Belyankin and Petrov, *Am. Mineral.*, **26**, 451 (1941).

II. Plazolite, Crestmore, California, recalculated from Foshag's analysis III, *Am. Mineral.*, **5**, 184 (1920), after deducting for admixed calcite indicated by the presence of CO<sub>2</sub>.

III. Composition corresponding to 3CaO · Al<sub>2</sub>O<sub>3</sub> · 2SiO<sub>2</sub> · 2H<sub>2</sub>O.

#### MATERIAL USED

Since Belyankin and Petrov had merely cast doubt on the composition assigned to the original hibsichte by Cornu, but contributed nothing to establish its composition or structure, and since it was reported by Cornu to be octahedral, in contrast to the dodecahedral habit of plazolite which is to be expected of a "grossularoid," it seemed desirable to the writer to reexamine the original hibsichte with a view of obtaining certainty in these matters. Through the courtesy of Dr. Foshag two specimens of hibsichte from Bohemia were borrowed from the collections of the United States National Museum.

All observations were made on a specimen labeled (USNM) "95150 Hibsichte microscopic crys. in enclosure of chalk-marl in phonolite. Aus-sig, Bohemia, Czecho-slovakia." It consists of several small fragments of pale-colored marl corresponding closely to the description given by Cornu. Even with a hand lens it is not possible to discern any hibsichte. The material to be studied was separated by prolonged leaching with cold, highly diluted, acetic acid, as described by Cornu. This tends to separate the hibsichte which is not attacked by such acid from the associated calcite and zeolites. Supplementing this treatment with light crushing, bromoform separation and prolonged picking under a binocular

microscope, concentrates of hibschite, containing several hundred crystals each, were made from two of the marl fragments. No differences were found in the appearance or properties of the hibschite in the two concen-

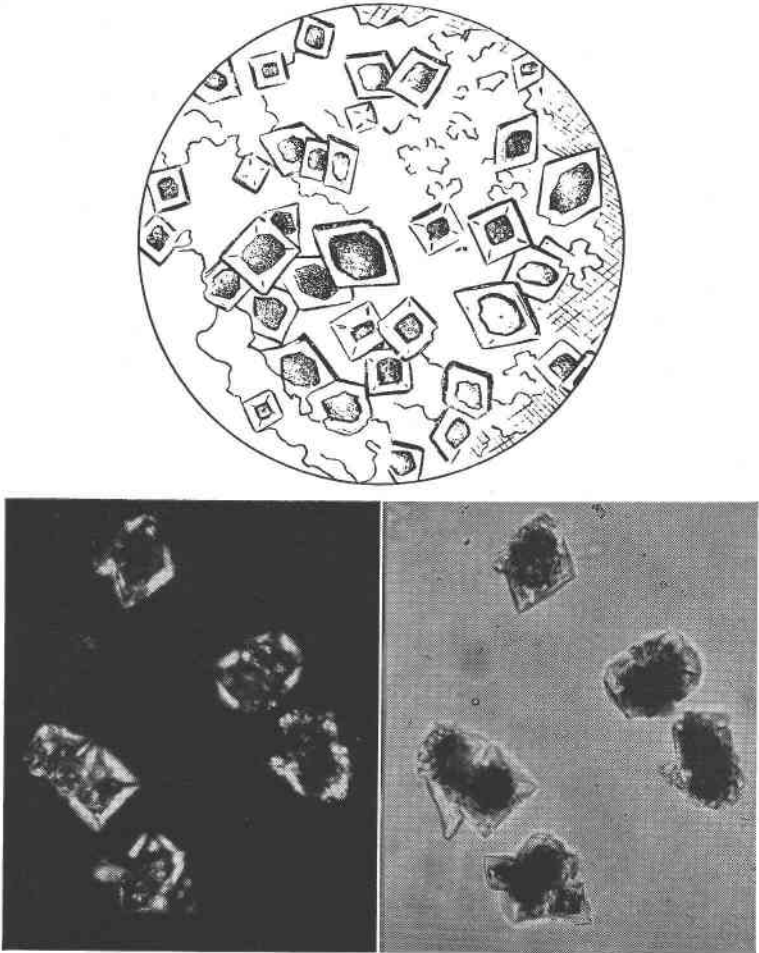


FIG. 1. Top: Cornu's Fig. 1, *Tsch. min., pet. Mitt.*, **25**, 256 (1906). Bottom: Hibschite crystals from Aussig, Bohemia, USNM 95150, in resin of  $n=1.67$ . Width of field 0.315 mm. Left, crossed nicols; right, same grains, nicols not crossed.

trates. Comparison of Cornu's drawing of hibschite, reproduced in the upper part of Fig. 1, with photomicrographs of crystals separated by the writer as described, shown in the lower part of Fig. 1, will leave no doubt that this is the material named hibschite by Cornu.

It was not possible to separate enough hibschite for a new analysis and besides all crystals showed cloudy nuclei of garnet from which they could not be separated. For this reason also it was impossible to determine satisfactorily the density of hibschite. The mixed grains, whose dimensions do not exceed 0.08 mm., were immersed in thallium formate solution and found to remain in suspension when the specific gravity of the solution was adjusted to 3.2–3.3. This is not in conflict with the reported specific gravities of hibschite and of the nuclei, but it does not exclude the possibility that the specific gravity of hibschite may be somewhat higher than 3.05, the figure reported by Cornu.

The thickness of the hibschite mantles varies greatly, but the mixed grains are always over half hibschite, and where the thickness of the mantle is about the same as the radius of the nucleus, as it is in many cases, the hibschite would constitute about seven-eighths of the volume of the grain.

The hibschite mantles are always quite clear and colorless, and show a slight birefringence, noted by Cornu, with a constant "quadrant structure," the vibration direction of the high index ray always being normal to the octahedral edges. Observation on many grains showed that the refractive index of the hibschite mantle is always about 1.69. This is considerably different from the value, 1.67, reported by Cornu, but only slightly higher than the values, 1.681 and 1.686, reported by Belyankin and Petrov for hibschite from near Nikortzmind, and from the Lopan gorge.

The garnet nuclei are all rather clouded and rough. Only a few grains were suitable for determination of the refractive indices of these nuclei. They were in all cases well below the index of methylene iodide saturated with sulphur. The mean index of these grains is probably of the order of 1.76–1.77. This is far below the value reported by Belyankin and Petrov, cited above. It would correspond to the index of garnets of composition about  $\text{Gr}_{80}\text{And}_{20}$ , which are well known, whereas the indices reported by Belyankin and Petrov would correspond to  $\text{Gr}_{53}\text{And}_{47}$ , an unlikely composition, or to a garnet of the Alm-Sp series which is not in harmony with the specific gravity of the material, the paragenesis, or the  $x$ -ray observations reported below. The garnet is certainly not melanite as stated by Cornu.

#### X-RAY EXAMINATION

Through the kindness of Mr. W. H. Dore of the Division of Plant Nutrition, College of Agriculture, University of California, the writer obtained an  $x$ -ray powder pattern of the hibschite with garnet nuclei. The 22 measurable lines of the powder pattern are recorded in Table 2. They

TABLE 2. POWDER PATTERN OF HIBSCHITE FROM NEAR AUSSIG, BOHEMIA.  
(USNM specimen 95150)

Mo-K $\alpha$  radiation; cassette radius, 8 inches.

Intensity	Sin <sup>2</sup> $\theta$	$(h^2+k^2+l^2)\times Q$	hkl
VW	0.00526	6 $\times$ 0.000877	211
S	0.01399	16 $\times$ 0.000875	400
VS	0.01741	20 $\times$ 0.000871	420
W	0.01915	22 $\times$ 0.000871	332
M	0.02093	24 $\times$ 0.000873	422
M-W	0.02268	26 $\times$ 0.000873	431
M	0.02623	30 $\times$ 0.000874	521
VW	0.02791	32 $\times$ 0.000872	440
M-S	0.03321	38 $\times$ 0.000874	611, 532
VW	0.03517	40 $\times$ 0.000879	620
M	0.04210	48 $\times$ 0.000877	444
M-S	0.04556	52 $\times$ 0.000876	640
S	0.04895	56 $\times$ 0.000874	642
M	0.05589	64 $\times$ 0.000874	800
M	0.06967	80 $\times$ 0.000871	840
M	0.07350	84 $\times$ 0.000875	842
W	0.07732	88 $\times$ 0.000879	664
VW	0.08607	98 $\times$ 0.000878	853, 941
W	0.10111	116 $\times$ 0.000872	10·4·0, 864
W	0.10562	120 $\times$ 0.000880	10·4·2
W	0.11264	128 $\times$ 0.000880	880
W	0.13432	152 $\times$ 0.000883	10·6·4

Average value of  $Q$ , 0.0008753

$$a_0 = 12.00 \pm 0.02 \text{ \AA}$$

VW very weak, W weak, M medium, S strong, VS very strong.

indicate an isometric body-centered cell with cube edge  $12.00 \pm 0.02 \text{ \AA}$ . This dimension is intermediate between those of the grossularite, plazolite and andradite cells, listed in Table 4.

Two phases are definitely present in this material, but all the lines of the powder pattern can be interpreted on the basis of one lattice and there is no indication (see Fig. 2) of the broadening or doubling of lines to be expected if two garnet-like materials of different cell dimensions were present. Hence it seems that the two phases have nearly the same cell dimensions.

The photometer curves of Fig. 2 show that the hibschite pattern is very similar to the patterns of plazolite and grossularite. In each case the high peak towards the right corresponds to (420) and the peak farthest to the left to (941) (853).

The slight intensity differences of plazolite and grossularite were dis-

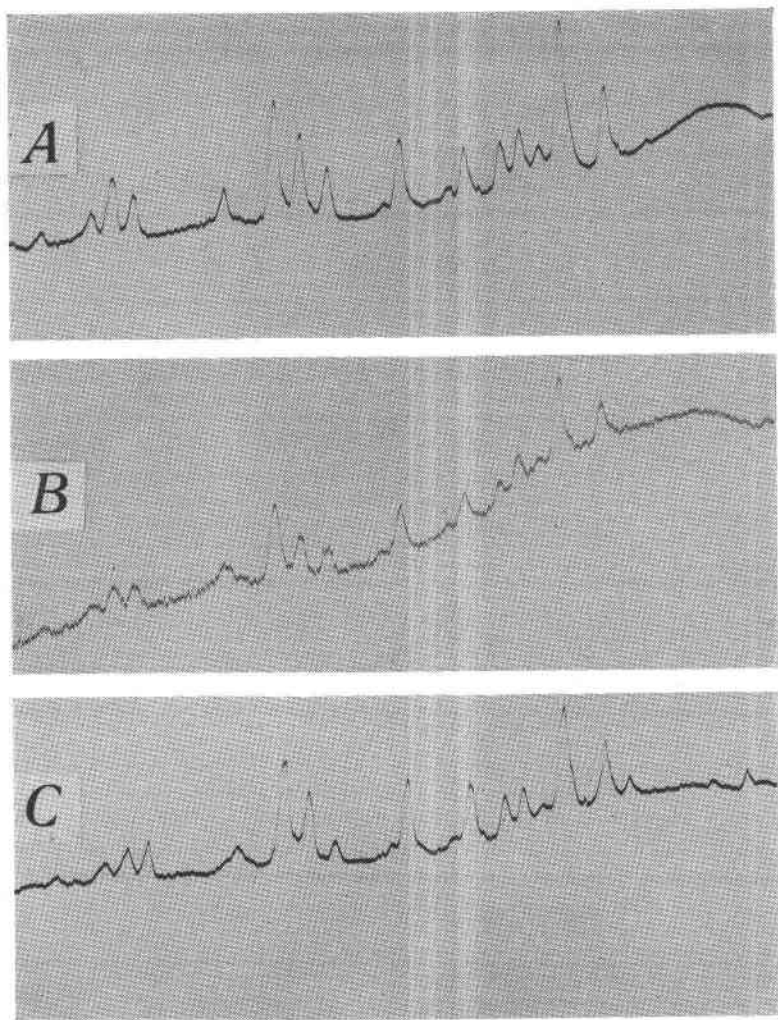


FIG. 2. Photometer curves of x-ray powder patterns. A—Grossularite, Georgetown, California; B—Hibschite, Aussig, Bohemia; C—Plazolite, Crestmore, California.

cussed by the writer<sup>10</sup> and it was shown that they can be accounted for by the structure proposed for plazolite. Close inspection of the photometer curves will show that the hibschite pattern shows intensity relations similar to, but not just like, either grossularite or plazolite. The most characteristic feature of the plazolite pattern, the small peaks for (211) and (321) at the right, is scarcely discernible in the hibschite pattern.

These observations can only be interpreted by a comparison with in-

<sup>10</sup> *Op. cit.*

tensities to be expected from the structures possibly present. Intensity calculations for garnets have been published by Menzer,<sup>11</sup> but are not wholly satisfactory because he did not use  $f$  curves. Stockwell<sup>12</sup> published nomograms for the powder patterns of garnets, but these indicate the intensity relations only very roughly. New calculations were made using the  $f$  curves of James and Brindley and estimated values of the scattering power of  $\text{Fe}^{III}$  as follows:—

$10^{-8} \times \sin \theta / \lambda$	0.0	0.1	0.2	0.3	0.4
$f_0 - \text{Fe}^{III}$	23.0	21.3	17.9	14.9	12.6

The results of these calculations, which are not far different from those

TABLE 3. INTENSITIES OF LINES IN POWDER PATTERNS.

	Andradite	Calculated* Grossularite	Plazolite	Observed Hibschite
211	0.00	0.02	0.39	VW
220	0.26	0.10	0.10	—
321	0.03	0.22	0.45	—
400	7.82	3.34	4.55	S
420	10	10	10	VS
332	0.55	0.86	0.34	W
422	5.49	2.59	1.40	M
431	1.49	1.42	1.85	M-W
521	1.41	1.73	2.62	M
440	0.00	0.42	0.38	VW
532	1.07	1.02	1.88	M-S
611	1.20	1.58	2.10	
620	1.68	0.00	0.59	VW
541	0.00	0.00	0.00	—
631	0.00	0.13	0.01	—
444	1.11	1.59	2.02	M
543	0.04	0.28	0.13	—
640	2.95	3.98	2.91	M-S
633	0.07	0.00	0.09	—
552	0.17	0.15	0.43	
721	0.00	0.00	0.00	
642	9.76	4.90	5.50	S
651	0.07	0.05	0.28	—
732	0.02	0.01	0.00	
800	2.16	1.38	1.58	M

\* Calculated intensities are on the basis of  $I_{420}$  taken as 10, this being the strongest line for all these materials in the range covered.

<sup>11</sup> Menzer, G., Die Kristallstruktur der Granate: *Zeits. Krist.*, **69**, 300–396 (1928).

<sup>12</sup> Stockwell, C. H., An  $x$ -ray study of the garnet group: *Am. Mineral.*, **12**, 327–344 (1927).



of Menzer and Stockwell just referred to, are given in Table 3 together with the observed intensities on hibschtite. It is clear from a comparison of the observed and calculated intensities that there cannot be any large contribution from an andradite (melanite) constituent, since this would require much greater intensity of (620) and other differences.

#### INTERPRETATION

All observations can be fairly well reconciled by considering hibschtite to be a material similar to plazolite, as proposed by Belyankin and Petrov. This would account for the values of the cell constants and indices shown in Table 4. The slightly higher indices of hibschtite doubtless arise from such differences in composition as are shown in Table 1.

TABLE 4.

	Lattice Constant	Refractive Index
1. Grossularite	11.840Å	1.735
2. Hibschtite, Marienberg	12.00	1.69
3. Hibschtite, Lopan gorge	—	1.686
4. Hibschtite, Nikortzmindia	—	1.681
5. Plazolite, Crestmore	12.14	1.675
6. Andradite	12.045	1.895

1. Values for pure grossularite, Fleischer, *Am. Mineral.*, **22**, 751-759 (1937).
2. Determined by writer on USNM specimen 95150.
- 3 and 4. Belyankin and Petrov, *Am. Mineral.*, **26**, 450-453 (1941).
5. Pabst, *Am. Mineral.*, **22**, 861-868 (1937).
6. Fleischer, *op. cit.*

As suggested above on the basis of their refractive indices, the nuclei of the hibschtite crystals are probably grossularite of a composition  $\text{Gr}_{80}\text{And}_{20}$ , within the range of known garnets. Garnets of this composition would have a cell constant, about 11.9Å, close to that determined from the hibschtite pattern. The difference, 0.1Å, is insufficient to produce doubling or even marked broadening of the lines, especially since the hibschtite portion probably makes up three fourths or more of the diffracting substance.

#### CRYSTAL HABIT

Though no crystals of hibschtite or plazolite have ever been found that are large enough for measurement, it is possible to determine the very simple forms without any doubt under a binocular microscope. Plazolite, like many garnets, shows dodecahedrons only. Hibschtite, on the other

hand, shows only octahedrons when the crystals are really well developed about small nuclei as at Marienberg, Nikortzinda, and the Lopan gorge. Only where it forms very thin crusts over dodecahedral nuclei, as at Mádstein and in some specimens from the Lopan gorge, is its outline dodecahedral, but in these cases the form must be largely controlled by the nuclei.

Crystals of garnet-like structure and octahedral habit are definitely anomalous. The reexamination of hibschite has revealed nothing to explain this anomaly.